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(54) METHOD OF PRODUCING UNSATURATED ALCOHOL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method of producing a high-purity unsaturated alcohol in good yield by suppressing side reactions caused by a double bond in the unsaturated alcohol when the unsaturation is reduced.

SOLUTION: An unsaturated aldehyde, an unsaturated fatty acid or an unsaturated fatty acid ester is hydrogenated using a zinc-chrome-based or a zinc- chromium-aluminum-based compound metal oxide catalyst to produce the unsaturated alcohol. In the process, the compound metal oxide catalyst having a content of copper contained in the compound metal oxide catalyst of ≤100 ppm expressed in terms of the metal and a content of nickel contained in the compound metal oxide catalyst of ≤200 ppm expressed in terms of the metal is used.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the manufacture approach of the unsaturated alcohol obtained in more detail by using a composite metallic oxide catalyst and carrying out partial saturation reduction of a partial saturation aldehyde, unsaturated fatty acid, or the unsaturated fatty acid ester about the manufacture approach of unsaturated alcohol.
[0002]
[Description of the Prior Art] The manufacture approach of unsaturated alcohol hydrogenates unsaturated fatty acid or unsaturated fatty acid ester under existence of a zinc-oxide-chrome oxide catalyst or a zinc-oxide-aluminum oxide as a catalyst in a ********** cage, for example, JP,45-2562,B, and the method of obtaining unsaturated alcohol is indicated. Moreover, in JP,54-36731,B, the metal catalyst of 4 yuan which consists of groups of a zinc oxide and/or cadmium oxide, an aluminum oxide, chromic oxide, and the barium oxide, or 5 yuan is indicated, and, on the other hand, the zinc-rare earth metal element is indicated as a catalyst by JP,58-210035,A.
[0003] However, when partial saturation reduction of unsaturated fatty acid ester was performed using these compound metal catalysts, it is very difficult to control the side reaction (for example, hydrogenation of a carbon-carbon double bond or transformer isomerization of a double bond) resulting from the double bond of unsaturated alcohol, and the problem had generated the rise of ****** of the obtained unsaturated alcohol, the fall of the iodine number, etc. in respect of purity.
[0004] On the other hand, the technique which controls hydrogenation of the double bond by JP,10-87534,A choosing a zinc oxide-titanium oxide metal catalyst is indicated. However, by this approach, while control of hydrogenation of a double bond is still inadequate, reference is not made at all by the problem of isomerization of a double bond.
[0005]
[Problem(s) to be Solved by the Invention] This invention is faced manufacturing unsaturated alcohol by partial saturation reduction, controls the side reaction (for example, hydrogenation of a double bond or isomerization of a double bond) resulting from the double bond of unsaturated alcohol, and aims at offering the approach of manufacturing the unsaturated alcohol of a high grade with sufficient yield.
[0006]
[Means for Solving the Problem] Artificers take lessons from the control approach of the side reaction at the time of carrying out partial saturation reduction using the composite metallic oxide catalyst of a zinc-chromium system, and pile up examination wholeheartedly. While the copper and/or the nickel component of a minute amount which are contained in the composite metallic oxide catalyst of zinc-KUROMU aluminum find out participating in side reaction, such as hydrogenation of a carbon-carbon double bond, and transformer isomerization By adjusting the content of these copper and/or a nickel component to below a constant rate, said side reaction can be reduced and it came to complete this invention based on the knowledge which is high yield, and finds out and starts that the unsaturated alcohol of the quality of an excellent article is obtained.

[0007] That is, the first purpose of this invention is to offer the manufacture approach of the unsaturated alcohol characterized by using the composite metallic oxide catalyst whose copper content which uses the composite metallic oxide catalyst of a zinc-chromium system or a zinc-chromium-aluminum system, faces hydrogenating a partial saturation aldehyde, unsaturated fatty acid, or unsaturated fatty acid ester, and manufacturing unsaturated alcohol, and is contained in a composite metallic oxide catalyst is 100 ppm or less in metal conversion and, whose nickel content is 200 ppm or less in metal conversion.
[0008] Zinc as a monoxide the second purpose of this invention 10 - 50 weight section, [a composite metallic oxide catalyst] It is the compound metallic-oxide molding catalyst which chromium becomes from 5 - 50 weight section, and aluminum becomes from the 0 - 100 weight section as 3 oxidation 2 aluminum as 3 oxidation Nichrome. Disruptive strength is [20 - 500 kg/cm3 or horizontal disruptive strength] 2-10kg per cm. And the compound metallic-oxide molding catalyst which has relative bulk density 1.0-1.8 is used. Under the condition which contains the methanol not more than 30 mol % in the high pressure gas which makes a subject the hydrogen in the reaction temperature of 200-350 degrees C, hydrogen pressure 100 - 400 kg/cm3, and a reactor, a partial saturation aldehyde, It is in offering the manufacture approach of unsaturated alcohol according to claim 1 characterized by hydrogenating unsaturated fatty acid or unsaturated fatty acid ester.
[0009] The third purpose of this invention is to offer the approach of controlling transformer isomerization of unsaturated alcohol characterized by using the composite metallic oxide catalyst of a zinc-chromium system or a zinc-chromium-aluminum system, facing hydrogenating a partial saturation aldehyde, unsaturated fatty acid, or unsaturated fatty acid ester, and manufacturing unsaturated alcohol, and setting the copper content in a composite metallic oxide catalyst to 100 ppm or less by metal conversion, and setting a nickel content to 200 ppm or less by metal conversion.
[0010]
[Embodiment of the Invention] As a composite metallic oxide catalyst whose copper content concerning this invention is 100 ppm or less in metal conversion and whose nickel content is 200 ppm or less in metal conversion, a zinc-chromium system composite metallic oxide catalyst or a zinc-chromium-aluminum system composite metallic oxide catalyst is mentioned.
[0011] Although it will not be limited as the manufacture approach of a composite metallic oxide catalyst that a copper content is 100 ppm or less in metal conversion, and a nickel content is 200 ppm or less in metal conversion especially if the content of copper and nickel is this within the limits, in the case of selection of a catalyst raw material, a copper content is 100 ppm or less in metal conversion per each raw material, and it is important that a nickel content chooses a thing 200 ppm or less by metal conversion.
[0012] Although it is thought that what is contained in the metal salt of the raw material used at the time of catalyst manufacture or a raw material metallic oxide is main as for the origin of these trace elements, mixing (for example, a manufacturing installation, manufacture water, the other things of the manufacturing facility origin) by contamination in the process at the time of catalyst manufacture can be considered besides it. Therefore, management is required also about the pollution control in process at the time of manufacture.
[0013] Approaches, such as the approach of reacting the sulfate or nitrate water solution, and alkali water solution of an approach, ** chromium, and zinc by the reaction of the ammonium water solution of an approach and ** dichromate which kneads ** zinc oxide with a chromic-acid water solution, a zinc sulfate, or a zinc nitrate water solution as the concrete manufacture approach of a composite metallic oxide catalyst that a copper content is 100 ppm or less in metal conversion, and a nickel content is 200 ppm or less in metal conversion, are illustrated.
[0014] Moreover, if a copper content is 100 ppm or less in metal conversion and a nickel content is 200 ppm or less in metal conversion, the raw material of a catalyst is not limited especially, either but can use well-known metallic compounds. Specifically, metal salts (the lead sulfate, the nitrate, a chromate, dichromate, a carbonate, a basic carbonate, a borate, etc. as a salt of a sulfate, a nitrate, a halogenide, and chromium as a zincky salt) or a metallic oxide, and a metal hydroxide are used as a raw material.
[0015] As a metal presentation of a zinc-chromium compound metallic oxide, 5 - 50 weight section is

illustrated [zinc] for chromium as a chromium trioxide to 10 - 50 weight section as a monoxide.
[0016] Moreover, it is possible to also obtain a zinc-chromium-aluminum compound metallic oxide by the same approach. As an aluminum component, a sulfate, a nitrate, or aluminum-oxide gel is used.
[0017] as the metal presentation of a zinc-chromium-aluminum compound metallic oxide -- zinc -- as a monoxide, 5 - 50 weight section and aluminum are illustrated as a chromium trioxide, and the 0 - 100 weight section is illustrated for 10 - 50 weight section and chromium as 3 oxidation 2 aluminum.
[0018] The compound metallic oxide obtained by the above-mentioned approach becomes usable as a catalyst for partial saturation reduction (hydrogenation) by calcinating after desiccation.
[0019] Furthermore, the above-mentioned catalyst may be cast to the powder of a compound metallic oxide at a suitable configuration using support with conventionally well-known binders, such as graphite, a silica, titanium oxide, a zirconium dioxide, a zeolite, etc. in order to raise the reinforcement.
[0020] Moreover, the above-mentioned composite metallic oxide catalyst can be used for hydrogenation also as a molding object also as powdered as the gestalt.
[0021] It is not limited especially as the shaping approach, for example, 5 or less % of the weight of graphite is mixed to composite metallic oxide catalyst powder, when required, after mixing and casting a chromic anhydride further, it is 250-750 degrees C preferably, and 50-800 degrees C is obtained by calcinating for 1 to 50 hours.
[0022] As for the acquired compound metallic-oxide molding catalyst, it is desirable that the disruptive strength of a catalyst is [20 - 500 kg/cm3 or horizontal disruptive strength] 2-10kg per cm, and it is recommended that disruptive strength is [50 - 350 kg/cm3 or horizontal disruptive strength] 3-10kg per cm more preferably.
[0023] Furthermore, as for the relative bulk density of a compound metallic-oxide molding catalyst, it is desirable that it is 1.0-1.8, and it is recommended that it is 1.05-1.5 more preferably.
[0024] As a hydrogenated raw material used by this invention, a partial saturation aldehyde, unsaturated fatty acid, unsaturated fatty acid ester, etc. can be illustrated. Specifically As a partial saturation aldehyde, the partial saturation aldehyde of carbon numbers 3-22 is illustrated. As unsaturated fatty acid The unsaturated fatty acid of carbon numbers 3-22 is illustrated. As unsaturated fatty acid ester The monoglyceride which has the alkyl ester of the unsaturated fatty acid of carbon numbers 3-22, alkenyl ester, or the partial saturation aliphatic series radical of carbon numbers 3-22, diglyceride, and a triglyceride are illustrated.
[0025] Moreover, as unsaturated alcohol obtained by this invention, the unsaturated alcohol of carbon numbers 3-22 is illustrated. The unsaturated alcohol of carbon numbers 10-22 is desirable, and oleyl alcohol is especially recommended.
[0026] As the reaction approach of hydrogenation, both the batch reaction approach and the successive reaction approach are usable, and although suitably chosen according to a volume etc., when industrialization level is taken into consideration, a successive reaction is desirable.
[0027] In the case of a successive reaction, it is possible to fill up a reactor with said catalyst, for example, to carry out by the reaction temperature of 200-350 degrees C, the hydrogen pressure force 100 - 400 kg/cm3.
[0028] furthermore, under a hydrogenation reaction -- a methanol -- 0 -- exceeding -- less than [30 mol %] -- when the hydrogen gas to contain is used, unsaturated alcohol is obtained more effectively.
[0029]
[Example] Hereafter, although an example explains this invention to a detail further, this invention is not limited to these examples.
[0030] In addition, in the following examples, various analysis adopted the following measuring methods.
[0031] The measuring method of copper or a nickel content: Carry out the quantum of this sample solution with an atomic absorption method after adding 2g of sodium peroxides to 1g (catalyst) of samples, carrying out heating fusion, adding a hydrochloric acid subsequently and considering as an acidic solution.
[0032] Catalyst reinforcement: Measure using a Kiya style hardness meter (large-sized) or a Kiya style

digital hardness meter (KHT-20) (all are Made in the Fujiwara Factory).
[0033] Relative bulk density: It is filled up with a catalyst to a 100ml graduation into a 100ml measuring cylinder, and measure the weight. The obtained weight of g/100ml serves as relative bulk density.
[0034] Saponification value: Measure mg of a potassium hydroxide which requires 1g of samples for saponifying completely based on a criteria fats-and-oils assay method.
[0035] hydroxyl value: -- mg of the potassium hydroxide required for neutralizing the acetic-acid radical of the acetylation object obtained from 1g of samples based on a criteria fats-and-oils assay method -- a number is measured.
[0036] Iodine number: Measure the amount of iodine added to the carbon-carbon double bond of a sample based on a criteria fats-and-oils assay method, and express with the weight percent to a sample.
[0037] HC content (hydrocarbon content): GC analyzes.
[0038] ******: Measure the temperature which cools a sample by part for 0.5-degree-C/, and begins to bloom cloudy based on a criteria fats-and-oils assay method.
[0039] Rate of elaidinization (rate of transformer isomerization) : GC analyzes.
[0040] Example 1 copper and nickel often kneaded 810g of zinc oxides of a low content, and 500g of chromic anhydrides by water 1000mL, it heated at 250 degrees C for 3 hours, and 40g graphite was further mixed after cooling, the hydrogen of per hour 30 L was processed 300 degrees C of delivery after making tablet molding (the path of 5mm, height of 5mm) for 3 hours, and 8kg per the average disruptive strength of 250kg/cm2 and average horizontal disruptive strength of 1cm and the molding catalyst of relative bulk density 1.14 were acquired. In metal conversion, 15 ppm and a nickel content are the same and the copper content of this molding catalyst was 20 ppm. The reaction cylinder (the bore of 2.2cm, height of 200cm) was filled up with this adjusted catalyst, and processing was carried out for hydrogen gas at 30 L/h delivery and 300 degrees C for 3 hours.
[0041] Next, the reaction cylinder was made into the reaction condition to which 240-260 degrees C and the 300kg/cm2 hydrogen containing methanol 20 mol % circulate, commercial olein acid methyl (saponification value 193.3, iodine number 86.5, acid number 3.8) was supplied by 450 mL/h, hydrogen gas was supplied at the preparation rate of 3Nm3/h (one atmospheric pressure, 0-degree-C conversion), partial saturation reduction was performed, and unsaturated alcohol was obtained. The quality of the obtained alcohol is shown in Table 1.
[0042]

表1 水素化還元後の分析値

反応例	使用した触媒		オレイルアルコールの品質					
	銅含量 (ppm)	ニッケル含量 (ppm)	ケン化価 (KOHmg/g)	水酸基価 (KOHmg/g)	ヨウ素価 (I_2／100g)	HC含量 (%)	曇り点 (℃)	エライジン化率 (%)
実施例1	15	20	5.4	203.1	92.8	0.5	1.5	0.08
実施例2	15	20	3.3	207.4	92.4	0.2	0.5	0.06
実施例3	20	60	3.8	206.8	92.2	0.7	2.1	0.08
比較例1	120	250	5.9	202.9	86.7	0.6	6.7	0.21
比較例2	180	270	4.1	205.9	84.3	0.8	8.5	0.33

[0043] Except having used oleic acid oleyl (saponification value 110.8, the iodine number 92.7, the acid number 0.05, hydroxyl value 6.1) as example 2 raw material, it carried out like the example 1 and oleyl alcohol was obtained. The quality is shown in Table 1.

[0044] Example 3 copper and nickel melted 1,488g of zinc nitrate and 6 hydrates of a low content, 1,876g of an amyl nitrate and 9 hydrates, and 2,000g of a chromium nitrate and 9 hydrates in the water of 10L, and melted and trickled 2,300g sodium carbonate into the water of 12L at this. The generated precipitate was calcinated at 400 degrees C a ** exception and after washing, 5% each of chromic anhydride and graphite were blended to the powder after cooling, it kneaded with little water, extrusion molding was carried out, and 300 degrees C was processed from the hydrogen of per hour 15 L for 8 hours. This molding catalyst was 10kg per average horizontal disruptive strength of 1cm, and relative bulk density 1.2. The copper content (metal conversion) of this molding catalyst was 20 ppm, and the nickel content (metal conversion) was 60 ppm. Using this molding catalyst, it carried out on the same

conditions as an example 1, and oleyl alcohol was obtained. The quality is shown in Table 1.
[0045] It carried out like the example 1 except having used the catalyst with an example of comparison 1 copper content [of 120 ppm] (metal conversion), and a nickel content (metal conversion) of 250 ppm. The quality of the obtained alcohol is shown in Table 1.
[0046] It carried out like the example 2 except having used the catalyst with an example of comparison 2 copper content [of 180 ppm] (metal conversion), and a nickel content (metal conversion) of 270 ppm. The quality is expressed to Table 1.
[0047]
[Effect of the Invention] According to this invention, the side reaction resulting from the double bond of unsaturated alcohol can be controlled, and the unsaturated alcohol of a high grade can be manufactured with sufficient yield.

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CLAIMS

[Claim(s)]
[Claim 1] The manufacture approach of the unsaturated alcohol characterized by using the composite metallic oxide catalyst whose copper content which uses the composite metallic oxide catalyst of a zinc-chromium system or a zinc-chromium-aluminum system, faces hydrogenating a partial saturation aldehyde, unsaturated fatty acid, or unsaturated fatty acid ester, and manufacturing unsaturated alcohol, and is contained in a composite metallic oxide catalyst is 100 ppm or less in metal conversion and, whose nickel content is 200 ppm or less in metal conversion.
[Claim 2] 10 - 50 weight section and chromium as 3 oxidation Nichrome as a monoxide 5 - 50 weight section, [a composite metallic oxide catalyst] [zinc] It is the compound metallic-oxide molding catalyst which aluminum becomes from the 0 - 100 weight section as 3 oxidation 2 aluminum. Disruptive strength is [20 - 500 kg/cm3 or horizontal disruptive strength] 2-10kg per cm. And the compound metallic-oxide molding catalyst which has relative bulk density 1.0-1.8 is used. Under the condition which contains the methanol not more than 30 mol % in the high pressure gas which makes a subject the hydrogen in the reaction temperature of 200-350 degrees C, hydrogen pressure 100 - 400 kg/cm3, and a reactor, a partial saturation aldehyde, The manufacture approach of unsaturated alcohol according to claim 1 characterized by hydrogenating unsaturated fatty acid or unsaturated fatty acid ester.
[Claim 3] How to control transformer isomerization of unsaturated alcohol characterized by using the composite metallic oxide catalyst of a zinc-chromium system or a zinc-chromium-aluminum system, facing hydrogenating a partial saturation aldehyde, unsaturated fatty acid, or unsaturated fatty acid ester, and manufacturing unsaturated alcohol, and setting the copper content in a composite metallic oxide catalyst to 100 ppm or less by metal conversion, and setting a nickel content to 200 ppm or less by metal conversion.

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